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STUDIES ON PULSE PLATING OF NICKEL WITH AND WITHOUT ADDITIVES

S MOHAN, R VENKATACHALAM AND K SRIVIDHYA

Central Electrochemical Research Institute, Karaikudi 630 006. INDIA

Pulsed electrolysis of nickel has been systematically investigated by electrodepositing nickel from a Watts type bath. Pulse cycles were changed from 10% to 80% and frequency was varied from 10 Hz to 100 Hz. Hull Cell experiments were conducted with both direct current and pulsed current. The effect of pulsed current on current efficiency and hardness of the deposit have been studied in detail. The effect of addition agents like saccharin on the deposit characteristics were studied.

Keywords : Nickel plating, pulse plating, additives.

INTRODUCTION

Recently pulse plating has been widely used for improving the properties of deposits [1]. The pulse plating has got many advantages such as enhanced plating rate in the case of copper deposited from sulfate solutions [2]; high purity gold deposits obtained from phosphate baths [3], pore free, high hardness cobalt deposits from sulfate baths [4] and reduced hydrogen embrittlement of zinc deposits obtained from cyanide electrolytes [5]. Improvements in micro throwing power and hardness when nickel is plated from a watts bath as reported in [6]. By using pulse reverse technique, crack free nickel coatings were produced from amide electrolytes [7]. Grain refinement of nickel deposited from sulfate solutions at high peak current densities wherein reduction in tensile stresses had occurred as reported in [8]. A detailed study of surface topography and microstructures of nickel deposited from electrolytes such as Watts, chloride and sulfamate baths was reported in [9]. Nanocrystalline nickel was reported to be produced by using pulse current [10].

In the current study, a systematic investigation of nickel deposition from a Watts-type nickel bath with saccharin as additive was undertaken with the application of square wave pulsed current. Hull Cell experiments were conducted with pulse current for the first time for optimizing plating current densities and the effect of pulse conditions on cathode current efficiency. The hardness of the deposit was compared with those for conventional direct current nickel deposits.

EXPERIMENTAL

An electrolyte consisting of $NiSO_4 . 6H_2O$ (240 g/l), $NiCl_2 . 6H_2O$ (45 g/l), H_3BO_3 (30 g/l) was prepared and purified by charcoal treatment and dummying at 0.5 A/dm^2. Deposition of nickel was carried out on copper cathodes (20 cm^2 area) after conventional pretreatment.

Hull Cell experiments were conducted in a 257 ml cell to choose the optimum average pulse current density. Pulse plating was carried out at 303 ± 1 K, using one liter of the electrolyte and employing "S" nickel anodes. Pulse frequencies of 10 to 100 Hz and duty cycles ranging from 10 to 80 percent were used. Details of pulse conditions were given in Tables I and II. Direct current (dc) experiments were also carried out for the purpose of comparison at a current density equal to the average pulse current density.

RESULTS AND DISCUSSION

Nickel deposits obtained at different cell current (dc) were shown in Figs. 1-3. The bright deposit was obtained at a frequency of 10 Hz (current 2A, 3A, 5A) at room

TABLE I: Details of pulse condition

Duty cycle (%)	Pulse frequency (Hz); Pulse on-off times (m.sec)		
	10	50	100
10	10-90	2-18	1-9
20	20-80	4-16	2-8
40	40-60	8-12	4-6
80	80-20	16-4	8-2

TABLE II: Details of pulse conditions at temp = 318 K

Pulse frequency (Hz)–			Current density (A/dm^2)	
10	50	100	Peak	Average
10-90	2-18	1-9	30, 50, 70	3, 5, 7
20-80	4-16	2-8	30, 50, 70	3, 5, 7
40-60	8-12	4-6	30, 50, 70	3, 5, 7
80-20	16-4	8-2	30, 50, 70	3, 5, 7

temperature. However at high temperature (318 and 323 K) the nickel deposit covered the entire surface indicating good coverage. At high currents (5A) burnt deposits were seen.

The Hull Cell pattern produced by different pulse condition were shown in Figs. 4-6. The bright deposit is obtained at a frequency of 10 Hz (current 2A. 3A, 5A) at room temperature without burnt deposits. However, on increasing frequency to 50 Hz and 100 Hz bright nickel deposits were obtained at high temperatures (318 K). At 100 Hz the nickel deposits covered the entire surface indicating good coverage.

At higher temperatures (318 and 323 K) only at 40% duty cycle bright nickel deposits were obtained (Fig. 7). When saccharin was added bright deposits are obtained at lower current under pulse conditions. But in dc such a behaviour was not observed (Fig. 8) At high temperature (318 K) under pulse condition bright deposits were obtained even at low duty cycle and low frequency. The Hull Cell patterns were shown in Fig. 9.

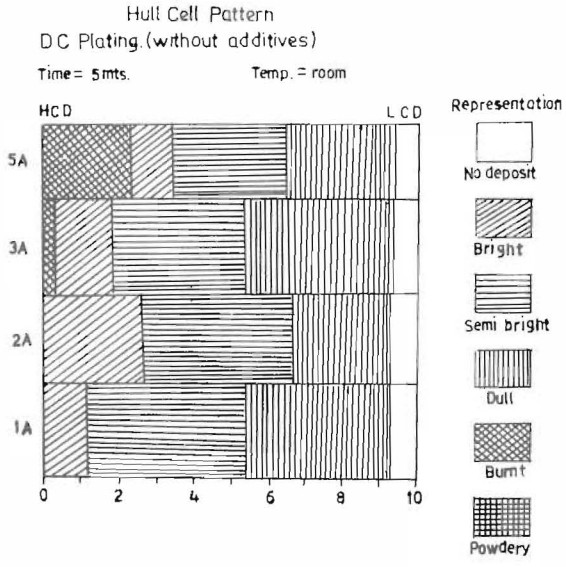

Fig. 1: Hull cell panels plated with nickel at different cell currents (DC) at room temperature

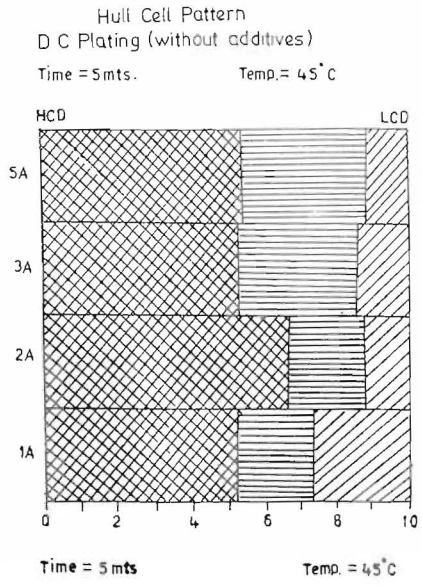

Fig. 2: Hull cell panels plated with nickel at different cell currentts (Temperature = 318 K, DC)

Effect of current density on cathode current efficiency

Fig. 10 shows the effect of current density on current efficiency. Current efficiency decreases with increasing current density, an effect which is usually observed in acid baths. The reason is that at high currents, evolution of hydrogen increases, resulting in reduction of the efficiency of nickel deposition.

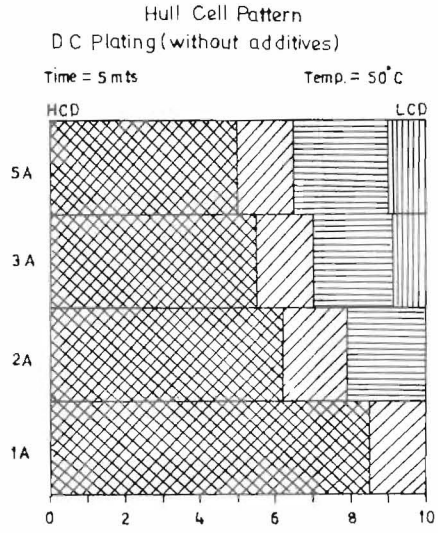

Fig. 3: Hull cell panels plated with nickel at different cell currents (Temperature = 323 K, DC)

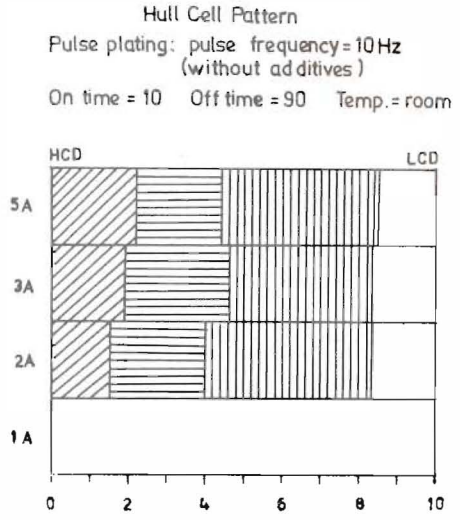

Fig. 4: Hull cell panels plated with nickel under different pulse conditions with pulse duty cycle 10% (Frequency = 10 Hz, Temperature = 308 K)

Effect of pulse duty cycle on cathode current efficiency

Higher current efficiency (96%) was recorded for deposition of nickel at 80% pulse duty cycle while at low duty cycle cathode current efficiency was lower (Fig. 11). At 5 A/dm^2 and at 7 A/dm^2 average pulse current density the current efficiency is increased with pulse duty cycle as shown in Fig. 12.

In pulsed deposition, although the average current density is similar to that in dc deposition, the corresponding peak currents are higher when the "current on" such high currents favour, more hydrogen evolution leading to reduction in

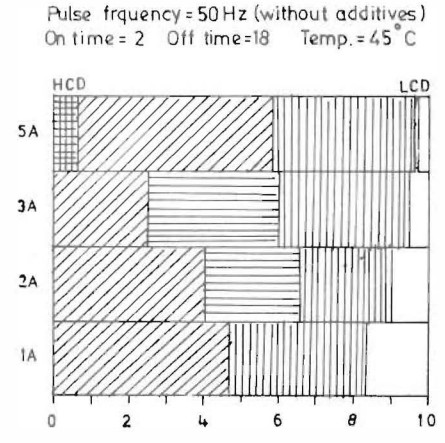

Fig. 5: Hull cell panels plated with nickel under different pulse conditions with pulse duty cycle 10% (Frequency = 50 Hz, Temperature = 318 K)

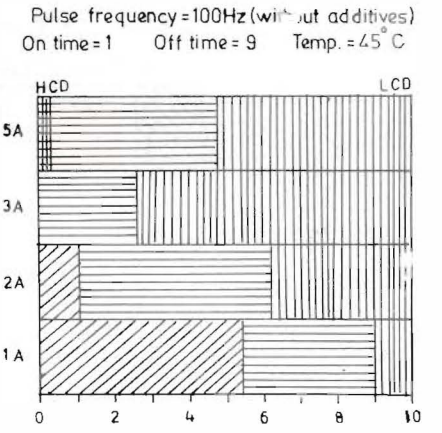

Fig. 6: Hull cell panels plated with nickel under different pulse conditions with pulse duty cycle 40% (Frequency = 100 Hz, Temperature = 318 K)

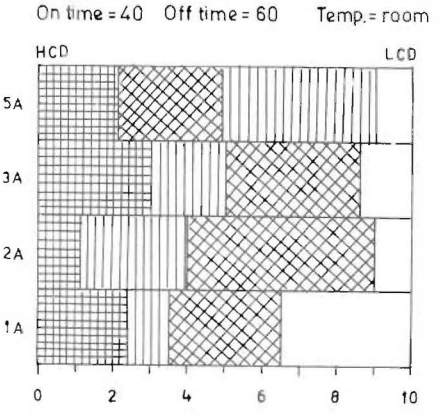

Fig. 7: Hull cell panels plated with nickel under different pulse conditions with pulse duty cycle 40% (Temp = 308 K)

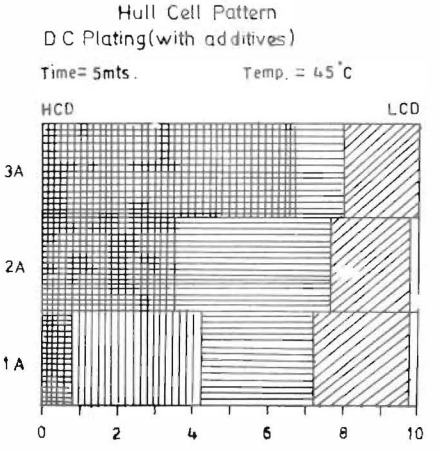

Fig. 8: Hull cell plated with nickel at different cell currents with saccharin (DC) Temperature = 318 K

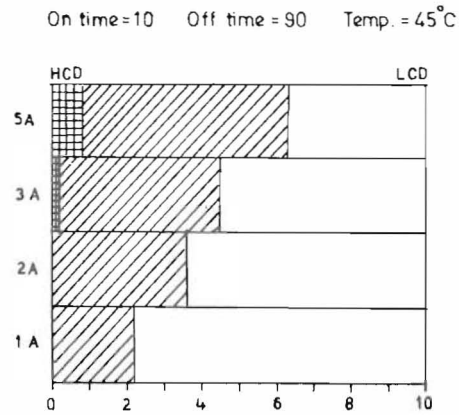

Fig. 9: Hull cell panels plated with nickel under different pulse conditions with saccharin (pulse duty cycle = 10% frequency = 10 Hz, temperature = 318 K)

cathode current efficiency for nickel deposit. Cathode current efficiency diminishes with pulse plating as a result of formation NiOHads in the deposition process. For nickel deposition the following mechanisms were proposed for Watts bath [11]

$$Ni^{2+} + H_2O \longrightarrow NiOH^+ + H^+$$

$$NiOH^+ + e^- \longrightarrow NiOH_{ads}$$

$$NiOH_{ads} + NiOH^+ + 3e^- \longrightarrow 2Ni + 2OH^-$$

Another suggested mechanism is [12]

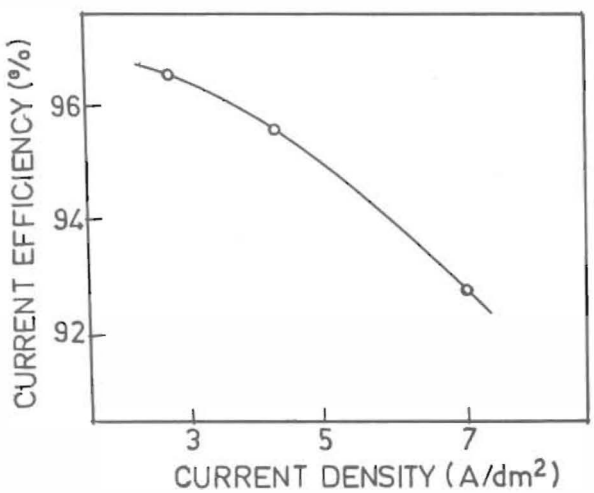

Fig. 10: Effect of current density on cathode current efficiency

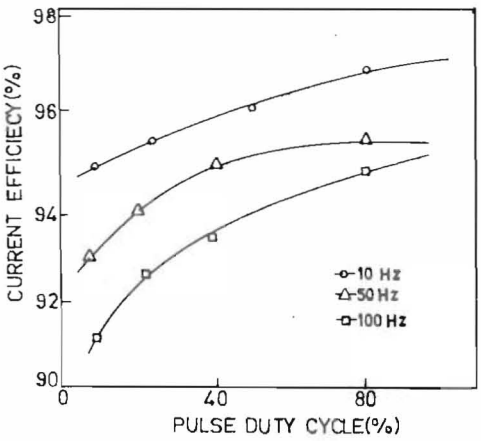

Fig. 11: Effect of pulse duty cycle on CCE at 3 A/dm^2 average current density

$$Ni^{2+} + H_2O \longrightarrow NiOH^+ + H^+$$

$$NiOH^+ + e^- \longrightarrow NiOH_{ads}$$

$$NiOH_{ads} + H^+ + e^- \longrightarrow Ni + H_2O$$

The overall reaction then becomes

$$Ni^{2+} + 2e^- \longrightarrow Ni$$

Both the above mechanisms proposed the formation of $NiOH_{ads}$ on the cathode surface, which was subsequently reduced to nickel atoms with cationic hydrogen in several Watts bath. The decline in cathode current efficiency with pulse plating as compared to dc is also a result of increase in discharge of hydrogen.

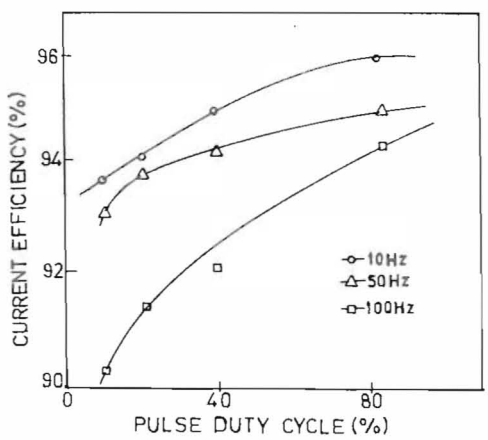

Fig. 12: Effect of pulse duty cycle on CCE at 5 A/dm^2 average current density

The following reaction mechanisms holds good and takes place when there is no current flowing [13]

$$Ni^{+} \longrightarrow Ni^{2+} + e^{-}$$

$$H^{+} + e^{-} \longrightarrow H_{ads}$$

$$NiOH + 2H^{+} \longrightarrow Ni^{2+} + H_{ads} + H_2O$$

Boric acid also plays an important role

$$H_3BO_3 \longrightarrow H^{+} + H_2BO_3^{-}$$

Boric acid is very good buffering agent that suppress the evolution of hydrogen. Because of this, the observed reduction in cathode current efficiency is small compared to dc deposition. The current-off period increases with decrease in pulse duty cycle. Accordingly there is sufficient time for the above reactions to take place, cathode current efficiency for nickel deposition decreases at low duty cycle.

Hardness of the deposit

Hardness of the nickel deposit is 190 HV in dc plating and 300 HV when nickel is deposited by pulse plating.

CONCLUSION

The pulsed electrodeposition of nickel at various duty cycle improved the hardness of nickel deposited from a Watts-type bath. The bright deposits were obtained without burnt deposit under pulse conditions at room temperatures compared to D.C. When saccharin was added, the bright deposits were obtained at low current, low duty cycle (318 K) . Under pulse conditions when compared to dc at 318 K the current efficiency of 97% I was obtained when the duty cycle was 80% and frequency was 10 Hz. When saccharin was added, brightness of deposit was increased. Therefore this study shows that nickel can be deposited upto a current density of 20 A/dm^2 under pulse conditions whereas in dc they can be deposited upto a current density of 5 A/dm^2. The hardness of nickel deposited by pulse plating was higher than obtained by direct current.

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